

Predicting Bioavailability of Sediment-Associated Organic Contaminants for *Diporeia* spp. and Oligochaetes

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Biota-sediment accumulation factors (BSAF) were calculated for *Diporeia* spp. and oligochaete worms exposed to polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) from field-collected sediment. These data were compared to the contaminant fraction extracted from sediment with Tenax resin using a 24 h extraction. A previous laboratory study suggested a linear relationship between log BSAF and the contaminant fraction rapidly desorbed from sediment. However, the BSAF data in our study did not fit this relationship. Better predictive regressions for both PCBs and PAHs were found when the log of the lipid-normalized organism contaminant concentrations were plotted against the log of the Tenax-extracted organic carbon-normalized sediment contaminant concentration. Regression lines for the two species had the same slope, but the *Diporeia* intercept was 2.3 times larger. When adjusted for a 6 h Tenax extraction, based on a regression between 6 and 24 h Tenax extractions, data from this study and two other studies that included multiple oligochaete species fit a single predictive regression. The exception included some PAHs that fell below the regression line. Thus, a single relationship generally predicted bioaccumulation across

sediments, compound classes, oligochaete species, and among laboratories.

Introduction

Determination of the bioavailability of sediment-associated organic contaminants has proven to be a difficult problem. Equilibrium partitioning theory (EPT) has served as the theoretical framework around which differences in bioavailability across sediments could be resolved for organic contaminants (1). However, chemical activity and bioavailability are influenced by many factors germane to the composition of organic matter in the sediment (2). Unfortunately, current geochemical isolation methods do not distinguish all of the relevant compositional variables important to bioavailability. Furthermore, the respective contaminant partition coefficients required to predict bioavailability are often unknown. For this reason, EPT is not always accurate (3).

Biomimetic extraction techniques using either solid-phase microextraction (SPME) (e.g., 4) or Tenax resin (e.g., 5) have proven to be equally useful for the description of the bioavailability of contaminants from sediments (6). The two methods use different approaches to arrive at the same experimental endpoint, a representation of the bioavailable contaminant pool in the sediment. SPME provides a surrogate approach to establish the equilibrium between the sediment and the organism through equilibrium between polydimethylsiloxane (PDMS) coated fibers and sediment (4). This presumably provides a measure of the freely dissolved porewater concentration based on PDMS–water partition coefficients. This technique has proven to be successful for the determination of the bioavailability of PAH, PCB, and DDT (4), TNT and its metabolites (7, 8), chlorobenzenes (9, 10) and PCB, and DDE, permethrin, and chlorpyrifos (6).

The Tenax approach measures desorption of contaminants from sediments, where the kinetics have often been found to be triphasic, by depletion of the contaminant pools at rates inversely related to contaminant–particle sorption strength (11). In that context, bioavailability has been linked to the fraction of contaminant that is rapidly desorbed (5, 12–14) or to a simplified Tenax extraction of 6 (15) or 24 h (13). For example, conducting a Tenax extraction for 6 h was found to represent approximately half of the amount of PAH, PCB, and chlorobenzenes rapidly desorbed (16). Similarly, a 24 h extraction was shown to directly approximate the fraction rapidly desorbed for selected PAH and PCB congeners (13, 14). Thus, Tenax extraction times of either 6 or 24 h could serve as simplified surrogates to represent contaminant bioavailability.

The objective of this work was to extend the use of Tenax biomimetic extractions to predict bioavailability. First, Tenax was tested as a biomimetic extractant for *Diporeia* spp. and mixed oligochaetes to compare bioaccumulation of PCBs and PAHs between genera. Second, Tenax extraction was used to predict bioavailability across sediments, oligochaete species, compounds, and field versus laboratory exposures.

Materials and Methods

Sediment and Animal Collections and Processing. *Diporeia* spp. and sediment were taken from three Lake Michigan stations in 2004. Oligochaete worms and sediments were collected at two of the stations that were resampled in 2005. Stations were chosen to have different sediment characteristics. Locations and contaminant concentrations are provided in Table 1.

Surficial sediment, *Diporeia* spp., and oligochaetes were collected using a stainless steel Ponar grab sampler. For *Diporeia*, the top 1–2 cm of sediment with the associated

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TABLE 1. Summary Characteristics of Stations and Organisms for Extracted Contaminants^a

station	latitude	longitude	water depth (m)	sediment PCB (ng/g dry weight)	sediment PAH (ng/g dry weight)	organic carbon (% of dry weight)	black carbon (% of dry weight)	Tenax PCB (ng/g dry weight)	Tenax PAH (ng/g dry weight)	organism PCB (ng/g dry weight)	organism PAH (ng/g dry weight)	lipid (% of dry weight)
<i>Diporeia</i>												
1	43° 15.83' N	86° 33.43' W	100	73.3 ± 1.6	3169 ± 45	2.61 ± 0.12	0.064 ± 0.014	9.15 ± 0.49	120.2 ± 9.7	332 ± 100	823 ± 41.5	10.78 ± 1.5
2	43° 12.0' N	86° 33.96' W	112	90 ± 1.4	3235 ± 121	2.65 ± 0.15	0.10 ± 0.01	12.3 ± 1.0	112.6 ± 6.6	271 ¹	534 ¹	11.97 ± 0.38
3	43° 21.33' N	86° 29.14' W	79	10.8 ± 0.23	1685 ± 642	0.46 ± 0.14	ND ^b	1.57 ± 0.24	24.9 ± 2.5	284.4 ± 46.8	1158 ± 415	17.1 ± 0.64
<i>oligochaete</i>												
1	43° 15.83' N	86° 33.43' W	100	78.2 ± 3.6	2785 ± 384	2.56 ± 0.06	0.057 ± 0.011	17.1 ± 2.2	154 ± 15.6	289 ± 129	440.1 ± 15.6	12.8 ± 1.8
2	43° 12.0' N	86° 33.96' W	112	118 ± 34.3	4005 ± 90	2.77 ± 0.04	0.066 ± 0.010	10.8 ± 4.4	91.6 ± 7.7	264 ± 37	541.9 ± 45.9	9.5 ± 1.0

^a PAH = polycyclic aromatic hydrocarbons, sum of fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]perylene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene; PCB = sum of 121 polychlorinated biphenyl congeners. Tenax indicates amount extracted by Tenax in 24 h normalized to the weight of sediment extracted. The standard deviation is indicated, and $n = 3$ for all data unless otherwise noted. ^b ND = not detectable.

organisms was collected with a stainless steel spatula and transferred to acetone-rinsed glass jars. For the oligochaetes, sediment for Tenax extraction and chemical analysis was collected as described above. In addition, 60 grab samples per station were washed through a 450 μ m net sieve, and the organisms and coarse sediment were placed in plastic bags with lake water. All samples were placed on ice for transport to the laboratory. Upon arrival at the laboratory, samples were kept at 4 °C until the sediment and animals could be separated the next day. The animals were removed from the sediment, rinsed with lake water, and frozen until analysis. A 6 h gut purging procedure was used for the oligochaete worms but was not necessary for the *Diporeia* because of their small digestive tract (17). Sediments were split into two subsamples: those for Tenax extraction were stored at 4 °C for ≤ 10 days prior to Tenax extraction. Those for chemical analysis were frozen (−20 °C) until chemical analysis (see Supporting Information for details).

Sediment and Animal Extractions. Extraction procedures for chemical analysis generally followed those outlined by Van Hoof and Hsieh (18, see Supporting Information for details). Thawed sediment and macerated organisms were dried with anhydrous sodium sulfate. Surrogates were added and samples were sonicated with methylene chloride. The samples were then concentrated, and solvent exchanged to hexane prior to further cleanup.

Contaminant Desorption (Extraction) using Tenax Resin. Tenax extraction was conducted in triplicate with each replicate consisting of a total of 30 g of wet sediment, which was divided into six subsamples of 5 g each. Sediment was weighed and placed into 50 mL round-bottom tubes, with 5 g in each tube. Acetone-rinsed and dried Tenax resin (1.25 g of Tenax-TA, 60/80 mesh, Scientific Instrument Services, Ringoes, NJ) was added to each 5 g of sediment. For blanks, the same amount of resin was added to each of three sets of six empty tubes. Then, 48 mL of filtered lake water and 1 mL of 1.25 mg/mL mercuric chloride, to prevent microbial degradation, were added to all tubes. The tubes were capped and rotated for 24 h.

Thereafter, the resin was separated from the sediment by repeatedly shaking the tubes and allowing the resin to float to the top of the water. Resin and a minimal amount of water was removed with a stainless steel scoop and rinsed into vials using acetone, approximately 5 mL per tube. The same surrogate standards were added to the resin/acetone mixture as for the other matrices. The sample vials were then capped and held at 4 °C for 24 h.

After 24 h, the acetone extract was removed, placed in separate vials, and stored at 4 °C. Nanograde hexane (5 mL) was added to the resin in each tube, mixed, and held for 24 h. The acetone and hexane extracts were combined, back-extracted into hexane, and the acetone/water mixture was discarded. The hexane extract was reduced in volume to 1 mL using nitrogen gas.

Sample Extract Clean Up. Columns containing deactivated alumina (10% water) and deactivated silica (3% water) were used for sample extract cleanup. The PCBs were eluted from the column with hexane, while the PAHs were eluted with hexane and 10% ether. The PCBs extracted from the sediment required treatment with activated copper to remove sulfur. Cleanup and quality control details are included in Supporting Information.

Contaminant and Organic Carbon Analyses. PCB congeners were analyzed by gas chromatography (GC) with electron-capture detection (19, Supporting Information Table TS-1), while 15 PAHs were analyzed with GC and mass-selective detection using selected-ion monitoring (see Supporting Information Table TS-2).

Sediment organic carbon (OC) analyses were performed using a carbon, hydrogen, and nitrogen (CHN) analyzer

(Model EA 1110 from CE Instruments, ThermoQuest Italia, Milan, Italy) after removal of carbonates with HCl. NIST certified standards with comparable percent OC were used to create calibration curves. These standards were analyzed with the samples. Samples for black carbon (BC) were determined following the method of Gustafsson et al. (20), with carbon content determined after preoxidation at 375 °C using the CHN analyzer.

Lipid analysis. Lipid content of the organisms was analyzed in triplicate using a spectrophotometric method after extraction with chloroform–methanol (21).

Statistics. Linear regression relationships were established using Systat (SPSS Inc, Chicago, IL). Significant differences between slopes and intercepts of regression lines were determined by analysis of covariance and differences in means using a t-test with Systat. Statistical significance was set at $p < 0.05$.

Results

Quality Control and Contaminant Concentrations. Spiked PCB recoveries for the matrix samples (sediment, tissue, and resin materials that were at background concentrations and used for spike recoveries, see Supporting Information for details) were very good (58–113%), except for PCB from oligochaete matrix tissues because of an error in spiking. However, the PCB surrogates from the oligochaete matrix had good average recovery 74% (see Supporting Information for details).

Total sedimentary PCB concentrations among the stations ranged from ~11 to 118 ng/g dry weight as the sum of detectable PCB congeners (Table 1). The mean PCB concentrations measured at stations 1 and 2 were not statistically different between years. Total sedimentary PAH concentration, reported as the sum of 15 compounds (Table 1) ranged from 1685 to 4005 ng/g dry weight. Station 1 data were not statistically different between the two collection years, while station 2 had a significantly higher concentration in the second year. The measured concentrations of OC and BC were similar in both collections (Table 1).

The total amount of PCBs extracted by Tenax resin in 24 h was different for station 1 between the 2 years with a greater amount extracted from the oligochaete collection (Table 1). In contrast, the amount of PAHs extracted by Tenax resin from stations 1 and 2 were not different across collection years (Table 1).

For the organisms, the concentrations of PCBs were similar between *Diporeia* and the oligochaetes collected from both stations 1 and 2. On the other hand, *Diporeia* accumulated approximately twice as much PAH as the oligochaetes collected from station 1 (Table 1). The lipid content of the two species was similar on a dry weight basis (Table 1). The comparability of the PCB data for the two organisms with similar lipid content supports our belief that the oligochaete tissue PCB data were not compromised despite the problems with the matrix recovery.

The fraction of contaminant extracted by Tenax resin in 24 h was expected to be similar in magnitude to the fraction of contaminant rapidly desorbed (13, 14) and represents a reasonable surrogate for the bioavailable fraction of an organic contaminant (14). This fraction ranged from ~10 to 60% of the total extractable PCB congeners and varied by congener. The fraction was much smaller for PAHs, ranging from ~1 to 6% of the total extractable PAHs from sediment and varied by compound. Thus, the PAHs should be less bioavailable than the PCBs by about a factor of 10 (see Supporting Information Tables TS-1 and TS-2).

Biomimetic Relationships. Species specific relationships between the lipid-normalized organism concentration plotted against the OC-normalized sediment concentration extracted with Tenax, both expressed on a log scale, were

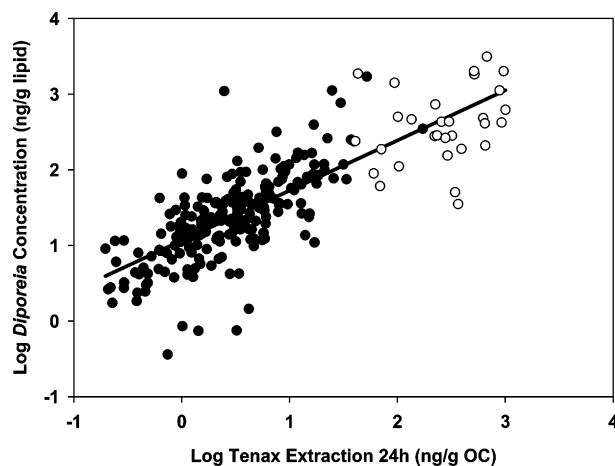


FIGURE 1. *Diporeia* spp. bioaccumulation on a lipid-normalized basis for polychlorinated biphenyl congeners (●) and polycyclic aromatic hydrocarbons (○) compared to the concentration extracted by Tenax in 24 h normalized to the organic carbon content of the sediment. The solid line is the regression line ($\log [Diporeia] = 0.663 \pm 0.032 \log [24 \text{ h Tenax extract}] + 1.062 \pm 0.035$, $r^2 = 0.630$, $n = 247$) through all the data.

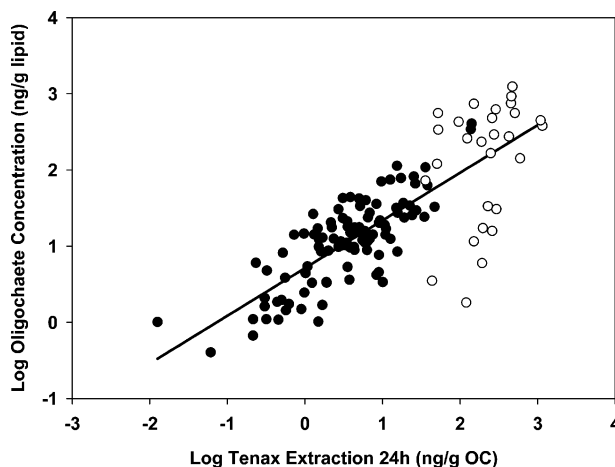


FIGURE 2. Mixed oligochaete bioaccumulation on a lipid-normalized basis for polychlorinated biphenyl congeners (●) and polycyclic aromatic hydrocarbons (○) compared to the concentration extracted by Tenax in 24 h normalized to the organic carbon content of the sediment. The solid line is the regression line ($\log [\text{oligochaete}] = 0.626 \pm 0.042 \log [24 \text{ h Tenax extract}] + 0.711 \pm 0.055$, $r^2 = 0.633$, $n = 131$) through all the data.

found for *Diporeia* and the oligochaetes (Figures 1 and 2). The data represent points where there were detectable concentrations in both Tenax and organisms. For the PCBs, 17% of the Tenax data points, mostly lower-chlorinated congeners, were not detectable in *Diporeia*. For the PAHs, 31% of the values with detectable Tenax concentrations were not detectable in *Diporeia*. A smaller number of data points were below detection, 7 and 10% for PAH and PCB, respectively, for the oligochaete tissues when concentrations were measured in Tenax extractions. Levels of PAHs and PCBs were not detectable in the organisms because of instrument detection limits and matrix interferences. The different percentages for *Diporeia* compared to those for the oligochaetes are the result of the relative sample sizes available for analysis, with oligochaete samples having about 5× greater mass. The slopes of the two regressions were not statistically different. However, the intercept for the *Diporeia* was 2.3 times larger than the intercept for the oligochaetes. Despite the generally similar lipid content, these two infaunal species exhibited different exposures. This was generally

thought to be caused by the differences in feeding behavior. *Diporeia* are very specific feeders (22), while the oligochaetes are expected to be more general feeders that are limited only by their mouth size (23).

Discussion

To use concentrations in Tenax directly as a surrogate for the bioavailable portion of a contaminant presumes that biotransformation does not affect the bioaccumulated residue. Surrogates such as Tenax and SPME apparatus are simple partitioning devices. Thus, if any organism biotransforms a contaminant then the amount extracted with Tenax or the SPME will be an overestimate of that contaminant's actual bioaccumulation. Biotransformation of PAHs is generally recognized, but the rate varies by species (24). PCBs are generally recognized as being far more recalcitrant, although biotransformation has been observed in a few instances with some specific congeners in fish (25). *Diporeia* spp. are not able to biotransform measurable quantities of PAHs (26). Thus it would not be reasonable to assume that this species has the ability to biotransform the more recalcitrant PCB congeners.

The ability of oligochaetes to biotransform PAHs is equivocal. *Lumbriculus variegatus* has been described as minimally capable of biotransforming PAH (27). However, another study suggests that *L. variegatus* has sufficient biotransformation capability to influence the bioaccumulation of phenanthrene (6). The oligochaetes in the Great Lakes study were mostly *Stylodrilus heringianus*, with *Limnodrilus hoffmeisteri*, *Potamothenix vejovskyi*, and *Tubifex tubifex* (28). One study with *S. heringianus* suggested that this organism has some ability to biotransform PAHs (29), but no studies with the other oligochaete species are available. The ability to biotransform PCBs was examined in *L. variegatus*. Neither the monochlorobiphenyl nor the dichlorobiphenyl, which should be more susceptible to biotransformation, were biotransformed (30). Since no other direct measures are available and because of the limited biotransformation of PAH for *S. heringianus*, which is similar to that of *L. variegatus*, it was assumed that PCBs would not likely be biotransformed by the Great Lakes oligochaetes in our study.

Bioavailability with BSAF. This study was designed as an attempt to confirm the laboratory findings of Kukkonen et al. (14), which demonstrated a regression between the log of the biota-sediment accumulation factor (BSAF, lipid-normalized concentration in the organism divided by the OC-normalized concentration in the sediment) and the fraction of contaminant rapidly desorbed from sediment. In that study, the 24 h extraction served as a surrogate for the amount of chemical in the rapidly desorbed pool (14). Fractions representing the rapidly desorbed contaminant (see Supporting Information Table TS-1 and TS-2) that were calculated as the concentration extracted with Tenax in 24 h, divided by the concentration in the sediment, both on an equivalent sediment basis. The PCB data from the field generally exceeded the estimates of bioavailability based on a laboratory regression model (14) (see Supporting Information Figures S1 and S2) for both species. This would suggest that the relationship between BSAF and fraction rapidly desorbed was not adequate for the description of bioavailability.

There are several reasons suspected for the failure of the laboratory regression to successfully predict BSAF from the field. For example, BSAFs are based on the concentration of contaminant in the bulk sediment. Both species feed selectively on fine particles (see above) that do not necessarily represent the bulk sediment concentration, thus these benthos should be exposed to differential amounts of sediment contaminants depending on feeding behavior.

Further, fractions of a contaminant associated with the bulk sediment may actually be physically occluded and hence, not available for assimilation. Thus, incorporation of the non-bioavailable fraction into the BSAF calculation introduces an experimental artifact. Finally, for PAHs in particular, biotransformation may affect the relationship between predicted and observed bioaccumulation, as discussed above, leading to low BSAF estimates. Thus, several unconstrained variables may hinder the accurate prediction of bioavailability via BSAF.

Tenax Regressions. On the basis of the information about biotransformation, it was expected that Tenax beads could be used as a proxy for the bioavailable contaminant concentration in sediment for the PCBs in both species and for the PAHs for *Diporeia* spp. and most likely for oligochaetes. Both PCB and PAH bioaccumulation was directly related to the concentration extracted with Tenax for *Diporeia* (Figure 1) and oligochaetes (Figure 2). This suggests that, for these sediments, predicting bioavailability via Tenax extractions overcomes any artifacts to the prediction of bioaccumulation created by strong contaminant-sorbing matrices in sediment such as BC (3, 31), which would introduce error into a BSAF calculation. The regression lines included both PCBs and PAHs. If only the PCB data were used, the lines would be statistically identical. The PAHs alone did not show good relationships with the amount extracted, which is likely due, in part, to the limited number of compounds represented and the variability in the data. For *Diporeia*, the data generally appear well scattered about the regression line suggesting that the scatter is largely caused by analytical variability rather than specific processes. The same cannot be said for the PAH in oligochaetes where there are eight points that are well below the regression line. Thus, the scatter around the regression line is uneven suggesting that biotransformation may have contributed in part to the observed data.

Prediction of Bioaccumulation Using a Broader Application of Tenax Extraction. In a recent study of both field and laboratory sediment bioaccumulation, data were found to fit on a single regression line (6) that plotted lipid-normalized organism concentrations versus Tenax-extracted OC-normalized sediment concentration. This suggested that it may be possible to fit the data from several studies to a single regression. Because a 6 h Tenax extraction is the norm for most bioaccumulation data in the literature (6, 15, 16), it was necessary to convert our Tenax extraction data to an equivalent 6 h extraction value. A linear regression relationship based on data by Kukkonen et al. (14) was used to interpolate from 24 h to 6 h. The Tenax desorption data (14) were fit with a regression that forced the intercept through zero. The resulting fraction extracted in 6 h was 0.54 ± 0.029 of the fraction extracted in 24 h. After correction of our 24 h-extracted concentration to the 6 h time point, all the data PCB congeners, along with the data from You et al. (6), provided a single regression ($\log [\text{biota}] = 0.916 \pm 0.028 \log [6 \text{ h Tenax extract}] + 0.853 \pm 0.038$, $r^2 = 0.893$, $n = 129$). A third data set (15), with data for six PCB congeners, hexachlorobenzene, DDD and DDE, and 12 PAH from either *Limnodrilus* spp. or *Lumbriculus rubellus*, was added to extend this comparison among species, compounds, across sediments, and laboratories. These data (15, excluding the PAHs) all plot on the same regression line as well (Figure 3). The lipid content of these oligochaetes (15) was determined gravimetrically from a 10/90 v/v acetone/hexane extraction. This different procedure apparently gave equivalent results to the spectrophotometric procedure used on this study (6) because the data cluster around the same regression line (Figure 3). Further, the PAH data for the *Limnodrilus* spp. (15) also plot on the regression line from the chlorinated hydrocarbon data (Figure 4). This suggests that *Limnodrilus* spp. do not readily biotransform PAH because biotransfor-

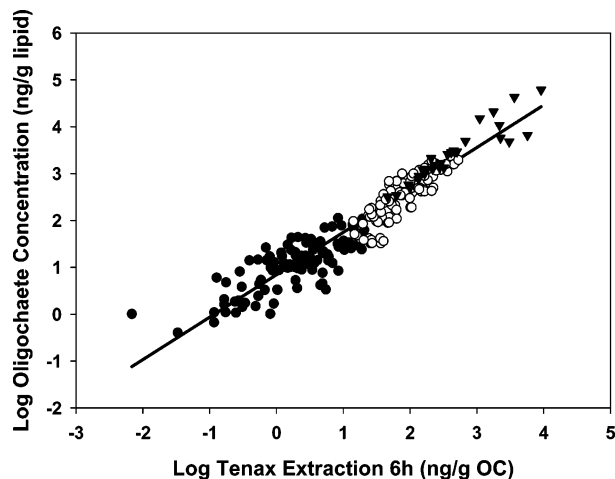


FIGURE 3. Comparison of the polychlorinated biphenyl data for mixed oligochaetes (●) and the mixed compound data for *L. variegatus* (▼) from You et al. (6) compared to chlorinated hydrocarbon data for polychlorinated biphenyl congeners, DDE, DDD, pentachlorobenzene, and hexachlorobenzene in two oligochaete species, *Limnodrilus* spp. and *L. rubellus* for 10 sediment and soil samples from ten Hulscher et al. (15, ○). A single regression line describes all the data ($\log [\text{biota}] = 0.912 \pm 0.021 \log [6 \text{ h Tenax extract}] + 0.835 \pm 0.033$, $r^2 = 0.897$, $n = 225$).

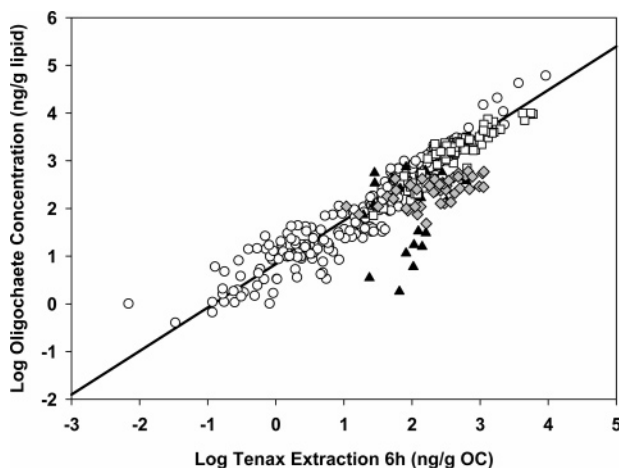


FIGURE 4. Comparison of the chlorinated hydrocarbon data from all studies (this study, 6, 15; ○, $\log [\text{biota}] = 0.912 \pm 0.021 \log [6 \text{ h Tenax extract}] + 0.835 \pm 0.033$, $r^2 = 0.897$, $n = 225$) with the polycyclic aromatic hydrocarbon data from the mixed Great Lakes oligochaetes (▲), *L. rubellus* (gray diamonds, 15), and *Limnodrilus* sp. (□, 15).

mation would cause the data to fall below the regression line that represents the more recalcitrant chlorinated compounds.

Because some of the bioaccumulation data for the PAHs fall below the regression line for the chlorinated compounds for some species, for example, mixed Great Lakes oligochaetes and *L. rubellus*, this suggests that some oligochaetes are capable of biotransformation. This supports the literature observations described above suggesting limited biotransformation by oligochaetes. Biotransformation is the most logical reason for data to fall below the regression line to predict bioaccumulation with Tenax extraction that is based primarily on chlorinated compounds which are not readily biotransformed. However, unrecognized analytical problems may also contribute to the data variance from the regression line created with recalcitrant compounds.

The ability of Tenax resin extraction to track the bioaccumulation of minimally biotransformed compounds across sediments, oligochaete species, experimental designs (labo-

ratory-spiked sediment, laboratory-exposed organisms to field collected sediment, and field-collected organisms), and among different laboratories is an important finding (Figure 3). The relationship is seemingly also applicable to PAHs and their bioaccumulation by *Limnodrilus* spp. (Figure 4). The relationship established for the chlorinated compounds among the various oligochaete studies provides a robust relationship that gives a maximum expected bioaccumulation and reflects the bioavailability from sediment. Even when bioaccumulation is reduced by biotransformation, as suggested by the PAH data that fall below the regression line for the recalcitrant compounds, the prediction from the regression line should predict expected exposure. Between-genera considerations will require development of specific regressions to reflect differences in apparent exposure conditions likely caused by differences in feeding behavior. However, the fact that the slopes are identical for the two genera examined suggests that the bioavailable fraction does not change. Thus, our study indicates that the concentration of a compound as determined by a 6 h Tenax extraction can be used as a proxy for the fraction of a compound in sediments that is rapidly desorbed and hence most bioavailable (14, 31).

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Supporting Information Available

Detailed methodology, quality control results, tables of the fractions of contaminant extracted by PCB congener and PAH, and figures of the BSAF versus fraction extracted for *Diporeia* spp. and oligochaetes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) DiToro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. A.; Paquin, P. R. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* **1991**, *10*, 1541–1586.
- (2) Accardi-Dey, A.; Gschwend, P. M. Reinterpreting literature sorption data considering both absorption onto organic carbon and adsorption onto black carbon. *Environ. Sci. Technol.* **2003**, *37*, 99–106.
- (3) Kukkonen, J. V. K.; Mitra, S.; Landrum, P. F.; Gossiaux, D. C.; Gunnarsson, J.; Weston, D. The contrasting roles of sedimentary plant-derived carbon and black carbon sediment-spiked hydrophobic organic contaminant bioavailability to *Diporeia* spp. and *Lumbriculus variegatus*. *Environ. Toxicol. Chem.* **2005**, *24*, 877–885.
- (4) Mayer, P.; Vaes, W. H. J.; Wijnker, F.; Legierse, D. C. H. M.; Kraaij, R. H.; Tolls, J.; Hermens, J. L. M. Sensing dissolved sediment porewater concentrations of persistent and bioaccumulative pollutants using disposable solid-phase microextraction fibers. *Environ. Sci. Technol.* **2000**, *34*, 5177–5183.
- (5) Kraaij, R. H.; Ciarelli, S.; Tolls, J.; Kater, B. J.; Belfroid, A. Bioavailability of lab-contaminated and native polycyclic aromatic hydrocarbons to the amphipod *Corophium volutator* relates to chemical desorption. *Environ. Toxicol. Chem.* **2001**, *20*, 1716–1724.
- (6) You, J.; Landrum, P. F.; Lydy, M. J. Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants. *Environ. Sci. Technol.* **2006**, *40*, 6348–6353.
- (7) Conder, J. M.; la Point, T. W. Solid phase microextraction of predicting the bioavailability of 2,4,6-trinitrotoluene and its primary transformation products in sediment and water. *Environ. Toxicol. Chem.* **2003**, *24*, 1059–1066.
- (8) Conder, J. M.; la Point, T. W.; Lotufo, G. R.; Steevens, J. A. Nondestructive direct-burial solid-phase microextraction fiber technique for measuring TNT in sediment. *Environ. Sci. Technol.* **2003**, *37*, 1625–1632.

- (9) Van der Wal, L.; van Gestel, C. A. M.; Hermens, J. L. M. Solid phase microextraction as a tool to predict internal concentration of soil contaminants in terrestrial organisms after exposure to a laboratory standard soil. *Chemosphere* **2004**, *54*, 561–568.
- (10) Van der Wal, L.; Jager, T.; Fleuren, R. H. L. J.; Barendregt, A.; Sinnige, T. L.; Van Gestel, C. A. M.; Hermens, J. L. M. Solid-phase microextraction to predict bioavailability and accumulation of organic micropollutants in terrestrial organisms after exposure to a field contaminated soil. *Environ. Sci. Technol.* **2004**, *38*, 4842–4848.
- (11) Cornelissen, G.; van Noort, P. C. M.; Govers, H. A. J. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax and effects of contact time and solute hydrophobicity. *Environ. Toxicol. Chem.* **1997**, *16*, 1351–1357.
- (12) Kraaij, R.; Seinen, W.; Tolls, J. Direct evidence of sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to benthic deposit feeders. *Environ. Sci. Technol.* **2002**, *36*, 3525–3529.
- (13) Shor, L. M.; Liang, W.; Rockne, K. J.; Young, L. Y.; Taghon, G. L.; Kosson, D. S. Intra-aggregate mass transport-limited bioavailability of polycyclic aromatic hydrocarbons to *Mycobacterium* strain PC01. *Environ. Sci. Technol.* **2003**, *37*, 1545–1552.
- (14) Kukkonen, J. V. K.; Mitra, S.; Landrum, P. F.; Gossiaux, D. C.; Gunnarsson, J.; Weston, D. The role of desorption for describing the bioavailability of select polycyclic aromatic hydrocarbon and polychlorinated biphenyl congeners for seven laboratory-spiked sediments. *Environ. Toxicol. Chem.* **2004**, *23*, 1842–1851.
- (15) ten Hulscher, T. E. M.; Postma, J.; den Besten, P. J.; Stroomberg, G. J.; Belfroid, A.; Wegener, J. W.; Faber, J. H.; van der Pol, J. J. C.; Hendriks, A. J.; van Noort, P. C. M. Application of Tenax extraction to measure bioavailability of sorbed organic contaminants to soil and sediment inhabiting organisms. *Environ. Toxicol. Chem.* **2003**, *22*, 2258–2265.
- (16) Cornelissen, G.; Rigterink, H.; ten Hulscher, T. E. M.; Vrind, B.; van Noort, P. C. M. A simple Tenax extraction method to determine the availability of sediment-sorbed organic compounds. *Environ. Toxicol. Chem.* **2001**, *20*, 706–711.
- (17) Lydy, M. J.; Landrum, P. F. Assimilation efficiency for sediment sorbed benzo(a)pyrene by *Diporeia* spp. *Aquat. Toxicol.* **1993**, *26*, 209–224.
- (18) Van Hoof, P.; Hsieh, J.-L. Extraction and cleanup of sediments for semivolatile organics following the internal standard method. In *Lake Michigan Mass Balance Study (LMMB) Methods Compendium Volume 2: Organic and Mercury Sample Analysis Techniques*; EPA905-R-97-012b; Great Lakes National Program Office, U.S. Environmental Protection Agency: Chicago, IL, 1997.
- (19) Van Hoof, P.; Hsieh, J.-L. Analysis of polychlorinated biphenyls and chlorinated pesticides by gas chromatography with electron capture detection. In *Lake Michigan Mass Balance Study (LMMB) Methods Compendium Volume 2: Organic and Mercury Sample Analysis Techniques*; EPA905-R-97-012b; Great Lakes National Program Office, U.S. Environmental Protection Agency: Chicago, IL, 1997.
- (20) Gustafsson, O.; Haghseta, F.; Chan, C.; Macfarlane, J.; Gschwend, P. M. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* **1997**, *31*, 203–209.
- (21) Van Handel, E. Rapid determination of total lipids in mosquitoes. *J. Am. Mosq. Control. Assoc.* **1985**, *1*, 302–304.
- (22) Harkey, G. A.; Lydy, M. J.; Kukkonen, J.; Landrum, P. F. Feeding selectivity and assimilation of PAH and PCB in *Diporeia* spp. *Environ. Toxicol. Chem.* **1994**, *13*, 1445–1455.
- (23) Brinkhurst, R. O.; Chua, K. E.; Kaushik, N. K. Interspecific interactions and selective feeding by tubificid oligochaetes. *Limnol. Oceanogr.* **1972**, *17*, 122–133.
- (24) Schuler, L. J.; Wheeler, A.; Bailer, A. K.; Lydy, M. J. Toxicokinetics of sediment-sorbed benzo(a)pyrene and hexachlorobiphenyl using the freshwater invertebrates *Hyalella azteca*, *Chironomus tentans*, and *Lumbriculus variegatus*. *Environ. Toxicol. Chem.* **2003**, *22*, 439–449.
- (25) Buckman, A. H.; Wong, W. S.; Chow, E. A.; Brown, S. B.; Solomon, K. R.; Fisk, A. T. Biotransformation of polychlorinated biphenyls (PCBs) and bioformation of hydroxylated PCBs in fish. *Aquat. Toxicol.* **2006**, *78*, 176–185.
- (26) Landrum, P. F.; Nalepa, T. F. A review of the factors affecting the ecotoxicology of *Diporeia* spp. *J. Great Lakes Res.* **1998**, *24*, 889–904.
- (27) Harkey, G. A.; Landrum, P. F.; Klaine, S. J. Comparison of whole-sediment, elutriate and pore-water exposures for use in assessing sediment-associated organic contaminants in bioassays. *Environ. Toxicol. Chem.* **1994**, *13*, 1315–1329.
- (28) Nalepa, T. F. Long-term changes in the macrobenthos of Southern Lake Michigan. *Can. J. Fish. Aquat. Sci.* **1987**, *44*, 515–524.
- (29) Frank, A. P.; Landrum, P. F.; Eadie, B. J. Polycyclic aromatic hydrocarbon rates of uptake, depuration, and biotransformation by Lake Michigan *Stylodrilus heringianus*. *Chemosphere* **1986**, *15*, 317–330.
- (30) Fisher, S. W.; Chordas III, S. W.; Landrum, P. F. Lethal and sublethal body residues for PCB intoxication in the oligochaete, *Lumbriculus variegatus*. *Aquatic. Toxicol.* **1999**, *45*, 115–126.
- (31) Cornelissen, G.; Gustafsson, Ö; Bucheli, T. D.; Jonker, M. T. O.; Koelmans, A. A.; Van Noort, P. C. M. Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **2005**, *39*, 6881–6895.

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